

Electro-chemical Sensor

The invention relates to a chemical sensor tool for use in downhole and methods for analyzing of fluids produced from subterranean formations. More specifically it relates to a
5 electro-chemical sensor for downhole pH and ion content analysis of effluents produced from subterranean formation.

BACKGROUND OF THE INVENTION

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Analyzing samples representative of downhole fluids is an important aspect of determining the quality and economic value of a hydrocarbon formation.

15 Present day operations obtain an analysis of downhole fluids usually through wireline logging using a formation tester such as the MDT TM tool of Schlumberger Oilfield Services. However, more recently, it was suggested to analyze downhole fluids either through sensors permanently or quasi-permanently
20 installed in a wellbore or through sensor mounted on the drillstring. The latter method, if successfully implemented, has the advantage of obtaining data while drilling, whereas the former installation could be part of a control system for wellbores and hydrocarbon production therefrom.

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To obtain an estimate of the composition of downhole fluids, the MDT tools uses an optical probe to estimate the amount of hydrocarbons in the samples collected from the formation. Other sensors use resistivity measurements to discern various
30 components of the formations fluids.

Particularly, knowledge of downhole formation (produced) water chemistry is needed to save costs and increase production at all stages of oil and gas exploration and production. Knowledge of
35 particularly the water chemistry is important for a number of key processes of the hydrocarbon production, including:

- Prediction and assessment of mineral scale and corrosion;
- Strategy for oil/water separation and water re-injection;
- Understanding of reservoir compartmentalization / flow units;
- Characterization of water break-through;

- 5 - Derivation of the water cut R_w ;and
- Evaluation of downhole the H_2S partition the oil and or water (if used for H_2S measurements).

10 Some chemical species dissolved in water (like, for example, Cl^- and Na^+) do not change their concentration when removed to the surface either as a part of a flow through a well, or as a sample taken downhole. Consequently information about their quantities may be obtained from downhole samples and in some cases surface samples of a flow. However, the state of chemical

15 species, such as H^+ ($pH = -\log[\text{concentration of } H^+]$), CO_2 , or H_2S may change significantly while tripping to the surface. The change occurs mainly due to a difference in temperature and pressure between downhole and surface environment. In case of sampling, this change may also happen due to degassing of a

20 sample (seal failure), mineral precipitation in a sampling bottle, and (especially in case of H_2S) - a chemical reaction with the sampling chamber. It should be stressed that pH , H_2S , or CO_2 are among the most critical parameters for corrosion and scale assessment. Consequently it is of considerable importance

25 to have their downhole values precisely known.

The concentration of protons or its logarithm pH can be regarded as the most critical parameter in water chemistry. It determines the rate of many important chemical reactions as well as the

30 solubility of chemical compounds in water, and (by extension) in hydrocarbon.

Hence, there is and will continue to be a demand for downhole

35 chemical measurements. However, no downhole chemical measurements actually performed in an oil and gas producing well

have been reported so far, though many different methods and tools have been proposed in the relevant literature.

General downhole measurement tools for oilfield applications are known as such. Examples of such tools are found in the United States Patents Nos. 6,023,340; 5,517,024; and 5,351,532 or in the International Patent Application WO 99/00575. An example of a probe for potentiometric measurements of ground water reservoirs is further published as: Solodov, I.N., Velichkin, V.I., Zotov, A.V. et al. "Distribution and Geochemistry of Contaminated Subsurface Waters in Fissured Volcanogenic Bed Rocks of the Lake Karachai Area, Chelyabinsk, Southern Urals" in: Lawrence Berkeley Laboratory Report 36780/UC-603(1994b), RAC-6, Ca, USA.

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The known state of the art in the field of high temperature potentiometric measurements and tool is described for example in the published UK patent application GB-2362469 A.

A number of chemical analysis tools are known from chemical laboratory practice. Such known analysis tools include for example the various types of chromatography, electrochemical and spectral analysis. Particularly, the potentiometric method has been widely used for the measurements of water composition (pH, Eh, H₂S, CO₂, Na⁺, Cl⁻ etc.) both in the laboratory and in the field of ground water quality control. US patent no 5,223,117 discloses a two-terminal voltammetric microsensor having an internal reference using molecular self-assembling to form a system in which the reference electrode and the indicator electrode are both on the sensor electrode. The reference molecule is described as a redox system that is pH-insensitive, while the indicator molecule is formed by a hydro-quinone based redox system having a potential that shifts with the pH. Both, reference molecule and indicator molecule layers are prepared by self-assembly on gold (Au) microelectrodes. In the known microsensor, a pH reading is derived from peak readings of the voltagrams.

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The laboratory systems, however, are often not suitable for wellbore application with demands for ruggedness, stability and low maintenance and energy consumption being rarely met.

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It is therefore an object of the present invention to provide apparatus and methods to perform electro-chemical measurements in hydrocarbon wells during drilling and production. More specifically, it is an object of the present invention to provide robust sensors for molecularly selective electro-chemical measurements, in particular pH measurements.

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SUMMARY OF THE INVENTION

15 The invention achieves its objects by providing an electro-chemical sensor having a measuring electrode with at least two receptors sensitive to the same species.

In a preferred variant of the invention the sensors are a redox system, based for example on anthraquinone chemistry.

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The substrate onto which the redox system is mounted is preferable based on carbon in one of its elementary forms such as graphite, carbon powder, diamond. In a variant of the invention the substrate may be derivatised nanotubes, including multi-walled nanotubes

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An electro-chemical technique using a method or sensor in accordance with the present invention can be applied for example as part of a production logging tool or an open hole formation tester tool (such as the Modular Dynamic Tester, MDT™). In the latter case, the technique can provide a downhole real-time water sample validation or downhole pH measurement which in turn can be used for predicting mineral scale and corrosion assessment.

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These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

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BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows a schematic diagram of the main elements of a known voltametric sensor;

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FIG. 2 shows a schematic diagram of the main elements of a known electro-chemical microsensor and its operation;

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FIG. 3 shows a schematic diagram of a known downhole probe using potentiometric sensors;

FIG. 4A illustrates the surface structure of a measuring electrode in accordance with an example of the invention;

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FIG. 4B illustrates the surface structure of a measuring electrode with internal reference electrode in accordance with another example of the invention;

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FIG. 4C illustrates the redox reaction of a measuring electrode in accordance with another example of the invention using multi-walled carbon nanotube;

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FIG. 4D illustrates the the redox reaction of a measuring electrode with internal reference electrode in accordance with another example of the invention using multi-walled carbon nanotube;

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FIG. 4E illustrates the geometrical surface layout of the electrode of FIG. 4B;

FIG. 5 is a perspective view, partially cut-away, of a sensor in accordance with an example of the present invention in a downhole tool;

5 FIG. 6 shows voltammograms recorded from an electro-chemical microsensor in accordance with the present invention at three different pH values;

FIG. 7A illustrates the shift of the peak potential for anthraquinone, diphenyl-p-phenylenediamine and a combination of the two redox systems;

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FIGS. 7B-C are plots of peak potential against pH for the redox systems of FIGS. 4C and 4D, respectively, over the pH range pH 1.0 to pH 12.0 at 293 K at various conditions;

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FIG. 8 illustrates an example of a sensor in accordance with the invention as part of a wireline formation testing apparatus in a wellbore;

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FIG. 9 shows a wellbore and the lower part of a drill string including the bottom-hole-assembly, with a sensor in accordance with the invention; and

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FIG. 10 shows a sensor located downstream of a venturi-type flowmeter, in accordance with the invention.

30 DETAILED DESCRIPTION OF THE INVENTION

The theory of voltammetry and its application to surface water measurements at ambient temperatures are both well developed. The method is based on the measurement of the electromotive force (e.m.f.) or potential E in a potentiometric cell which includes measuring and reference electrodes (half-cells).

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FIG. 1 shows the general components of a known voltammetric cell **10**. A measuring electrode **11** is inserted into a solution **13**. This electrode consists of an internal half element (for example, Ag wire covered by an AgCl salt) in a solution of a fixed pH (for example, 0.1M HCl in some pH electrodes), and an ion-selective membrane **111** (like glass H⁺ selective membrane in pH glass electrode). The reference electrode **12** also contains an internal half-element (typically the same AgCl;Ag) inserted in a concentrated KCl (for example 3M) solution / gel saturated with Ag⁺, which diffuses (or flows) through the reference (liquid) junction **121**.

The ion-selective electrode **11** measures the potential that arises because of the difference in activity or concentration of a corresponding ion (H⁺ in case of pH) in the internal solution and in the measured solution. This potential is measured against the reference potential on the reference electrode **12**, which is fixed because of a constant composition of a reference solution / gel. The electrodes may be separated (separate half cells), or combined into one ("combination electrode").

The measured e.m.f. is an overall function of the temperature and the activity of an *i*th ion, to which the measuring electrode is selective:

$$[1] \quad E = E^0 + (k \cdot T) \cdot \log(a_i),$$

where *E* is the measured electromotive force (e.m.f.) of the cell (all potentials are in V), *a_i* corresponds to the activity of the *i*th ion and is proportional to its concentration. *E*⁰ is the standard potential (at temperature *T*) corresponding to the *E* value in a solution with the activity of *i*th ion equal to one. The term in parenthesis is the so-called Nernstian slope in a plot of *E* as a function of log(*a_i*). This slope (or the constant "k") together with the cell (electrode) constant (*E*⁰) is experimentally determined via a calibration procedure using standard solutions with known activities of *i*th ion. For good

quality undamaged electrodes this slope should be very close to the theoretical one, equal to $(R \cdot T / F \cdot z)$, where F is the Faraday constant (23061 cal/mole), R is the gas constant (1.9872 cal/mole K), z_i is the charge of i th ion.

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The Nernst equation [1] can be rewritten for pH sensors, i.e. $\log a(H^+)$ as

$$[2] \quad E_{0.5} = K - (2.303 RTm/nF)pH$$

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where $E_{0.5}$ is the half-wave potential of the redox system involved, K is an arbitrary constant, R is the ideal gas constant, m is the number of protons and n is the number of electrons transferred in the redox reaction.

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The microsensor of US patent no 5,223,117 is illustrated in FIG. 2. FIG. 2A. shows a schematic electro-chemical sensor with a counter electrode **21** and a relatively much smaller (by a factor of 1000) Au substrate **22** that carries two molecular species M and R . The R species forms an inert reference electrode, and species M is an indicator electrode with specific receptors or sensitivity for a third species L . The schematic linear sweep voltammogram in the upper half of FIG 2C shows the difference in the current peaks for the oxidization in the normal state. When
20 the third species L binds to M (FIG. 2B), this difference increases as illustrated by the shift of peaks in the lower half of FIG. 2C, thus providing a measure for the concentration of L in the solution surrounding the sensor. In the context of the present invention, it is important to note that the R is
25 specifically selected to be insensitive to the species L , e.g. pH.
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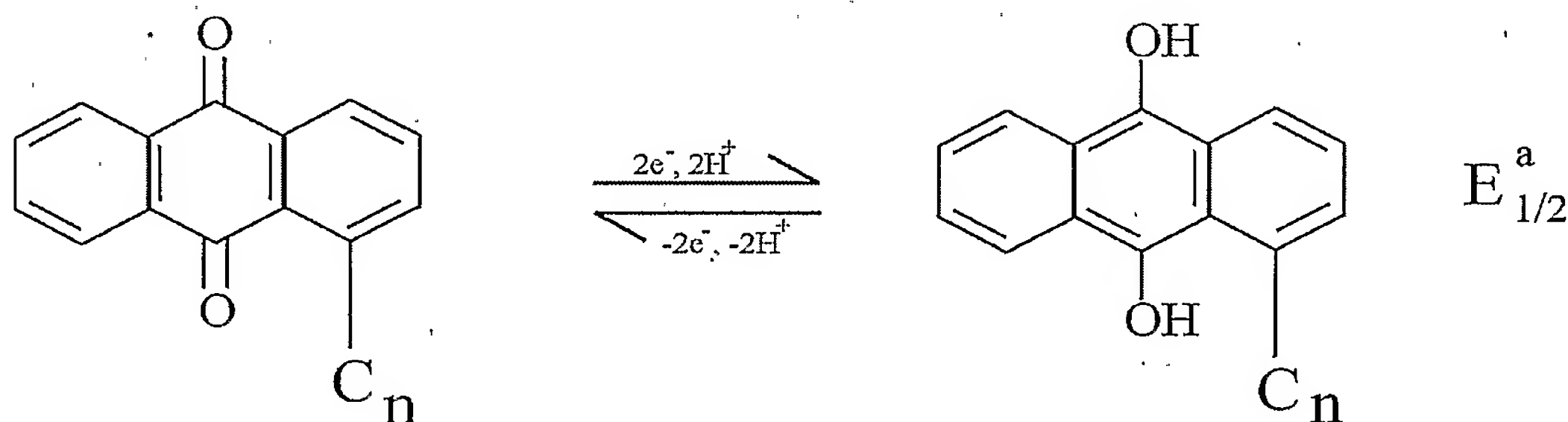
In FIG. 3, there are schematically illustrated elements of a known downhole analyzing tool **30** as used by Solodov et al (see
35 background). The body of the tool **30** is connected to the surface via a cable **31** that transmits power and signals. A computer console **32** controls the tool, monitors its activity and records

measurements. The tool **30** includes a sensor head with a number of selective electro-chemical probes **33** each sensitive to a different molecular species. Also housed in the body of the tool are further actuation parts **34** that operate the head, a test system **35** and transceivers **36** to convert measurements into a data stream and to communicate such data stream to the surface. The electrodes are located at the bottom part of the probe and include those for pH, Eh (or ORP), Ca^{2+} (pCa), Na^+ (pNa), S^{2-} (pS), NH_4^+ (pNH₄), and reference electrode (RE). H_2S partial pressure may be calculated from pH and pS readings.

In the following aspects and elements of the present invention are described in detail.

The present invention introduces a new molecular system in which the redox features of two molecules are combined, thus leading to a considerably higher accuracy and, in turn, downhole deployability.

In a preferred embodiment for a pH sensitive sensor an anthraquinone is homogenously derivatised onto carbon particles (AQC)

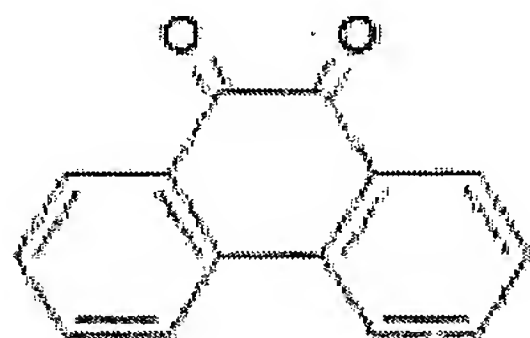


The AQC system is derived using 2g of carbon powder (1.5 μm in mean diameter) mixed with a 10 cm^3 solution containing 5 mM Fast Red AL Salt (Anthraquinone-1-diazonium chloride) to which 50 mM hypophosphorous acid (50%) is added. The reaction is allowed to stand with occasional stirring at 5 $^{\circ}\text{C}$ for 30 minutes, after which it is filtered by water suction. Excess acid is removed by washing with distilled water and with the powder being finally

washed with acetonitrile to remove any unreacted diazonium salt in the mixture. It is then air dried by placing inside a fume hood for a period of 12 hours and finally stored in an airtight container.

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In a similar manner, phenanthrenequinone (PAQ)

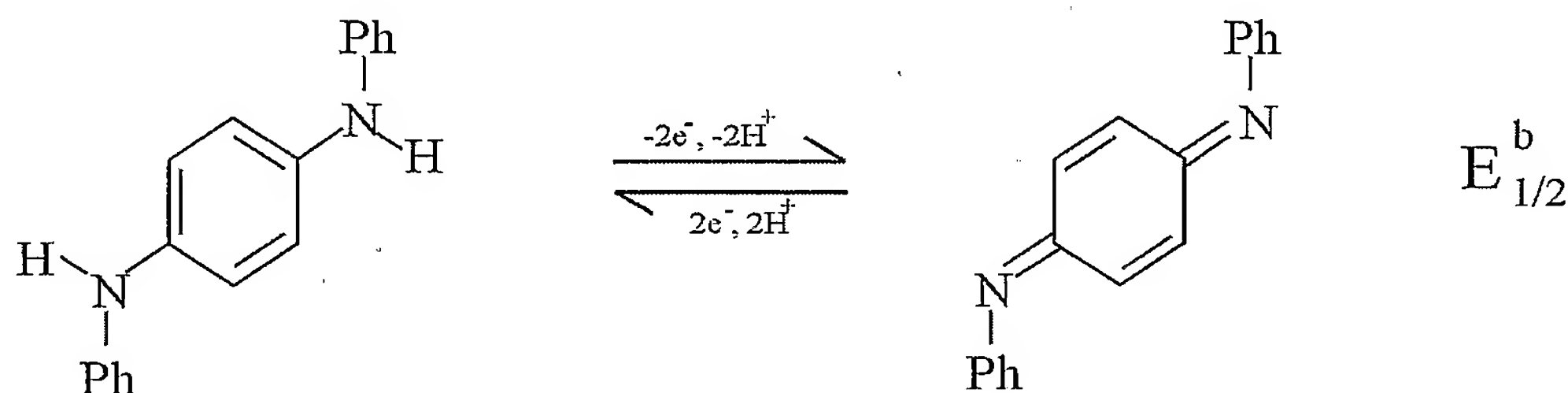


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Is prepared as a second molecular species to undergo a redox reaction

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Alternatively, N,N'-diphenyl-p-phenylenediamine (DPPD) spiked onto carbon particles undergoes a redox process as shown below:



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The bonding of DPPD onto carbon is achieved by mixing 4 g of carbon powder with 25mL of 0.1M HCl + 0.1M KCl and 20mM DPPD solution in acetone. The reaction mixture is stirred continuously for 2 hours in a beaker and then filtered after which it was washed with distilled water to remove excess acid and chloride. It is then air dried by placing inside a fume hood for 12 hours and finally stored in an airtight container.

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In a static environment where the sensor surface is not exposed to a flow, it is possible to immobilize water insoluble DPPD crystals directly onto the electrode surface. However in the

wellbore environment it is preferred to link the sensitive molecules via a chemical bond to such surface.

The derivatised carbon powders are abrasively immobilised onto a basal plane pyrolytic graphite (BPPG) electrode prior to voltammetric characterisation following a procedure described by Scholz, F. and Meyer, B., "Voltammetry of Solid Microparticles Immobilised on Electrode Surfaces in Electroanalytical Chemistry" ed. A.J. Bard, and I. Rubenstein, Marcel Dekker, New York, 1998, 20, 1. Initially the electrode is polished with glass polish paper (H00/240) and then with silicon carbide paper (P1000C) for smoothness. The derivatised carbons are first mixed and then immobilised onto the BPPG by gently rubbing the electrode surface on a fine qualitative filter paper containing the functionalised carbon particles.

The resulting modified electrode surface is schematically illustrated by FIG. 4A showing an electrode **41** with bonded DPPD and AQC.

It is further advantageous too add an internal pH reference involving a pH independent redox couple to increase the stability of any voltammetric reading, hence circumventing uncertainties caused by fouling of the external reference electrode. In the configuration, the sensor includes two reference electrodes.

A suitable reference molecule is, for example, $K_5Mo(CN)_8$ or polyvinylferrocene (PVF) which both have a stable redox potential ($K_5Mo(CN)_8$ at around 521 mV) that is sufficiently separated from expected shifting of redox signals of the two indicator species over the pH range of interest. As shown in Table 1 that both the oxidation and reduction potentials of $K_5Mo(CN)_8$ are fairly constant across the entire pH range of interest.

TABLE 1

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pH	AQ _{OX}	AQ _{RED}	DPPD _{OX}	DPPD _{RED}	Mo- _{OX}	Mo- _{RED}
4.6	- 0.440	- 0.448	0.202	0.224	0.524	0.524
6.8	- 0.576	- 0.580	0.094	0.082	0.528	0.522
9.2	- 0.710	- 0.674	- 0.204	-0.372	0.512	0.508

10 The Mo-based reference species can be retained in the solid substrate via ionic interactions with co-existing cationic polymer, such as poly (vinyl pyridine), that was spiked into the solid phase. Other pH independent species, such as ferrocyanide are less suitable as the redox peaks are obscured by the signals of the measuring redox system.

15 In FIG 4B the electrode **42** carries bonded molecules AQC and PAQ together with PVF as an internal reference molecule.

The most common forms of conducting carbon used in electrode manufacture are glassy carbon, carbon fibres, carbon black, various forms of graphite, carbon paste and carbon epoxy. One further form of carbon, which has seen a large expansion in its use in the field of electrochemistry since its discovery in 1991 is the carbon nanotube (CNT). The structure of CNTs approximates to rolled-up sheets of graphite and can be formed as either single or multi-walled tubes. Single-walled carbon nanotubes (SWCNTs) constitute a single, hollow graphite tube. Multi-walled carbon nanotubes (MWCNTs) on the other hand consist of several concentric tubes fitted one inside the other.

The above activation methods for binding a redox active species to graphite or carbon surfaces can be extended via the chemical reduction of aryldiazonium salts with hypophosphorous acid, to include the covalent derivatisation of MWCNTs by anthraquinone-1-diazonium chloride and 4-nitrobenzenediazonium tetrafluoroborate. This results in the synthesis of 1-anthraquinonyl-MWCNTs (AQ-MWCNTs) and 4-nitrophenyl-MWCNTs (NB-MWCNTs) as shown in FIGs. 4C and 4D, respectively. The respective substrates **46** and **47** are multi-walled carbon nanotubes.

The preparation process of the derivatised MWCNT involves the following steps: first 50 mg of MWCNTs are stirred into 10 cm³ of a 5 mM solution of either Fast Red AL (anthraquinone-1-diazonium chloride) or Fast Red GG (4-nitrobenzenediazonium tetrafluoroborate), to which 50 cm³ of hypophosphorous acid (H₃PO₂, 50% w/w in water) is added. Next the solution is allowed to stand at 5 °C for 30 minutes with gentle stirring. After which, the solution is filtered by water suction in order to remove any unreacted species from the MWCNT surface. Further washing with deionised water is carried out to remove any excess acid and finally with acetonitrile to remove any unreacted diazonium salt from the mixture. The derivatised MWCNTs are then air-dried by placing them inside a fume hood for a period of 12 hours after which they are stored in an airtight container prior to use. Untreated multi-walled nanotubes can be purchased from commercial vendors, for example from Nano-Lab Inc of Brighton, MA, USA in 95% purity with a diameter of 30+/-15 nm and a length of 5-20 µm.

The reduction of diazonium salts using hypophosphorous acid as demonstrated is a versatile technique for the derivatisation of bulk graphite powder and MWCNTs. This has the advantage over previous methods involving the direct electrochemical reduction of aryldiazonium salts onto the electrode surface, as our chemically activated method allows the possibility for inexpensive mass production of chemically derivatised nanotubes

for a variety of applications. Furthermore the derivatisation of MWCNTs proffers the possibility of sensor miniaturisation down to the nano-scale.

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In FIG. 4E there is shown a possible geometric configuration or layout for the sensor surface **40** which is exposed to the wellbore fluid. The surface includes a working electrode **43** as described in FIGs. 4A or 4B, together with the (external) reference electrode **44** and a counter electrode **45**.

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A schematic of a microsensor **50** incorporating a modified surface prepared in accordance with the procedure described above is shown in FIG. 5. The body **51** of the sensor is fixed into the end section of an opening **52**. The body carries the electrode surface **511** and contacts **512** that provide connection points to voltage supply and measurement through a small channel **521** at the bottom of the opening **52**. A sealing ring **513** protects the contact points and electronics from the wellbore fluid that passes under operation conditions through the sample channel **53**.

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It is an advantage of the new sensor to include two measuring or indicator electrodes or molecules measuring two e.m.f or potentials with reference to the same reference electrode and being sensitive to the same species or molecule in the environment. As a result the sensitivity towards a shift in the concentration of the species increases. Using the above example of AQC and DPPA and the pH (or H^+ concentration, the Nernst equation applicable to the new sensor is the sum of the equations describing the individual measuring electrodes. Thus, combining the half wave potential $E_{0.5}(AQC)$ for anthraquinone

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$$[3] \quad E_{0.5}(AQC) = K(AQC) - (2.303 RT_m/nF)pH$$

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with the half wave potential $E_{0.5}(DPPD)$ for N,N'-diphenyl-p-phenylenediamine

$$[4] \quad E_{0.5}(\text{DPPD}) = K(\text{DPPD}) - (2.303 \text{ RTm/nF})\text{pH}$$

yields the half wave potential $E_{0.5}(\text{S})$ for the combined system:

$$\begin{aligned}
 5 \quad E_{0.5}(\text{S}) &= E_{0.5}(\text{AQC}) + E_{0.5}(\text{DPPD}) = \\
 [5] \quad (K(\text{AQC}) + K(\text{DPPD})) - 2*(2.303 \text{ RTm/nF})\text{pH} &= \\
 K(\text{S}) - 2*(2.303 \text{ RTm/nF})\text{pH}
 \end{aligned}$$

Where $K(\text{S})$ is the sum of the two constants $K(\text{AQC})$ and $K(\text{DPPD})$.

10 As the shift of the potential with a change in pH depends on the second term, the (theoretical) sensitivity of the sensor has doubled.

The use of a further (third) redox system sensitive to the same species would in principle increase the sensitivity further. As the method detects shifts in the peak location of the voltammogram, however, more efforts are anticipated to be required to resolve overlapping peaks in such a three-molecule system.

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FIG. 6 shows results in a range of pH solutions (pH 4.6, 0.1M acetic acid + 0.1M sodium acetate buffer; pH 6.8, 0.025M disodium hydrogen phosphate + 0.025M potassium dihydrogen phosphate buffer; pH 9.2, 0.05M disodium tetraborate buffer). The figure presents the corresponding square wave voltammograms when the starting potential was sufficiently negative to have both DPPD and AQ in their reduced forms.

FIG. 7A depicts the relationship between the redox potential and pH for both the DPPD (▪) and AQ (♦). The plot reveals a linear response from pH 4 to 9 with a corresponding gradient of ca 59 mV/pH unit (at 25°C) which is consistent with an n electron, m proton transfer where n and m are likely to be equal to two. By combining the two individual curves in a manner as described in equation [5], a new function (▲) is derived with a superior sensitivity for the species to be detected.

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For the two activated MWCNT species described above, the peak potential using cyclic voltammetry (CV) is found to be pH-dependant. This voltammetric behaviour is consistent with previous studies of carbon powder covalently modified with 1-anthraquinonyl groups and can be attributed to the two-electron, two-proton reduction/oxidation of the 1-anthraquinonyl moiety to the corresponding hydroquinone species.

When NB-MWCNTs is studied a more complicated voltammetric pattern can be observed. Upon first scanning in a reductive fashion a large, electrochemically irreversible peak is observed (labelled as system I), the exact peak potential of which depends on the pH studied. When the scan direction is reversed and swept in an oxidative fashion a new peak at more positive potentials than the irreversible peak is observed, which upon repeat cycling was found to behave in an electrochemically reversible fashion as the corresponding reduction wave was observed. This system is labelled as system II. Again the exact peak potential of system II is found to vary with the pH studied. This behaviour is consistent with the reduction mechanism, of the nitro moiety in aqueous media as exemplified by nitrobenzene in FIG. 4D. It is worth noting that all subsequent characterisation procedures for NB-MWCNTs are carried out on system II, which corresponds to the reversible aryl nitroso/aryl hydroxylamine couple, after several initial scans are performed to form this redox couple.

When investigating the effect of pH of AQ-MWCNTs and NB-MWCNTs over the range pH 1.0 to pH 12.0 using CV and square wave voltammetry (SWV) at room temperature as well as the behaviour of AQ-MWCNTs at elevated temperatures up to 70 °C. SWV was used because it provides us with a sharp, well-defined peak in a single sweep. As concomitant proton loss/gain occurs on oxidation/reduction of AQ-MWCNTs or NB-MWCNTs (see FIGs. 4C and 4D respectively) the peak potential depends on the local proton concentration, i.e. pH, as described by the Nernst equation [6]:

$$[6] \quad E_{\text{peak}} = E_{\text{formal}}^0 - \frac{2.3RTm}{nF} \text{pH}$$

where m and n, the number of protons and electrons transferred respectively, are both likely to be equal to two in the case of AQ-MWCNTs and the aryl nitroso/arylhydroxylamine couple in the case of NB-MWCNTs. The formulation [6] of the Nernst equation is equivalent to those of equations [1] and [2].

At room temperature the peak potentials for both AQ-MWCNTs and NB-MWCNTs are found to shift to more negative potentials with increasing pH as predicted. A corresponding plot of peak potential against pH was found to be linear over the entire pH range studied in all cases (see FIGs. 7B and 7C, respectively) and a comparison of the gradient of the plots of peak potential vs. pH are found to be close to the ideal value of 58.1 mV/ pH unit with the exception of the irreversible peak (system I) for NB-MWCNTs which was found to shift by only 37.6 mV / pH unit.

The response of AQ-MWCNTs to pH at elevated temperatures up to 70 °C is studied using SWV. Note that the pH of the solutions used may vary with temperature, and so to this end three IUPAC buffers with a known pH at each temperature studied were employed. These are the pH 4.6, pH 6.8 and pH 9.2 buffers. The Nernst equation predicts that the peak potential should shift to more negative values as the temperature is increased due to the temperature dependence of the formal potential (E_{peak}^0). Figure 7D does indeed reveal that as the temperature is increased the peak potential is shifted to more negative values. However, in contrast to the behaviour of carbon powder covalently derivatised with the anthraquinonyl moiety (AQcarbon) where the peak currents increase steadily with increasing temperature after an initial increase in peak current up to ca 40 °C, the peak currents for AQ-MWCNTs gradually decreases with increasing temperature. This behaviour has also been previously observed for MWCNT agglomerates at elevated temperatures. The temperature invariance of derivatised MWCNTs is not fully understood but has

a potential advantage for pH sensors which are required for use in elevated temperature environments.

In FIG. 7E there is illustrated the effect of varying pH at room temperature for molecular anthraquinone in the solution phase versus the AQ-MWCNTs immobilised onto a bppg electrode. 1 mM anthraquinone solutions are prepared at each pH and studied using cyclic voltammetry at a bare bppg electrode. The variation of peak potential with pH for both cases over the pH range 1.0 to 14.0 are studied with additional experiments carried out at pH 10.5, pH 13.0 and pH 14.0. The plot of peak potential versus pH for both 1mM anthraquinone in solution and for the immobilised AQ-MWCNTs reveals that, in the case of AQ-MWCNTs, a linear response is observed over the entire pH range studied. However for the anthraquinone in the solution phase, the plot is no longer linear above ca. pH 10.5 (FIG. 7E). This can be attributed to the pKa for the removal of the first proton, pK_{a1} , of the reduced form of anthraquinone (see FIG. 4C) in solution being ca. $pK_{a1} = 10$. The pKa for the removal of the second proton is ca $pK_{a2} = 12$. At higher pHs than pH 10 the reduced form of anthraquinone may be deprotonated causing a change in the variation of peak potential with pH. No such deviation from linearity is observed for the AQ-MWCNTs. From this it can be concluded that derivatisation onto the surface of the MWCNTs may change the pK_a of the anthraquinonyl moiety. This clearly demonstrates that derivatisation onto MWCNTs proves advantageous to the analytical sensing of pH as the pH window for use is favourably widened for derivatised AQ-MWCNTs compared to free anthraquinone in solution.

Analysis of the peak potential as a function of pH at each temperature shows good agreement between the experimental and theoretically predicted values thereby showing the mechanism can be readily used as a simple, inexpensive pH probe, which works over a wide range of temperatures.

The novel probe may be placed inside various wellbore tools and installations as described in the following examples.

5 In FIGs. 8-11 the sensor is shown in various possible downhole applications.

In FIG. 8, there is shown a formation testing apparatus **810** held on a wireline **812** within a wellbore **814**. The apparatus **810** is a well-known modular dynamic tester (MDT, Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky U.S. Pat. No. 3,780,575 to Urbanosky and Pat. No. 4,994,671 to Safinya et al., with this known tester being modified by introduction of an electro-chemical analyzing sensor **816** as described in detail above (FIG 8). The modular dynamics tester comprises body **820** approximately 30m long and containing a main flowline bus or conduit **822**. The analysing tool **816** communicates with the flowline **822** via opening **817**. In addition to the novel sensor system **816**, the testing apparatus comprises an optical fluid analyser **830** within the lower part of the flowline **822**. The flow through the flowline **822** is driven by means of a pump **832** located towards the upper end of the flowline **822**. Hydraulic arms **834** and counterarms **835** are attached external to the body **820** and carry a sample probe tip **836** for sampling fluid. The base of the probing tip **836** is isolated from the wellbore **814** by an o-ring **840**, or other sealing devices, e.g. packers.

Before completion of a well, the modular dynamics tester is lowered into the well on the wireline **812**. After reaching a target depth, i.e., the layer **842** of the formation which is to be sampled, the hydraulic arms **834** are extended to engage the sample probe tip **836** with the formation. The o-ring **840** at the base of the sample probe **836** forms a seal between the side of the wellbore **844** and the formation **842** into which the probe **836** is inserted and prevents the sample probe **136** from acquiring fluid directly from the borehole **814**.

Once the sample probe **836** is inserted into the formation **842**, an electrical signal is passed down the wireline **812** from the surface so as to start the pump **832** and the sensor systems **816** and **830** to begin sampling of a sample of fluid from the formation **842**. The electro-chemical detector **816** is adapted to measure the pH and ion-content of the formation effluent.

A bottle (not shown) within the MDT tool may be filled initially with a calibration solution to ensure in-situ (downhole) calibration of sensors. The MDT module may also contain a tank with a greater volume of calibration solution and/or of cleaning solution which may periodically be pumped through the sensor volume for cleaning and re-calibration purposes.

Electro-chemical probes in an MDT-type downhole tool may be used for the absolute measurements of downhole parameters which significantly differ from those measured in samples on the surface (such as pH, Eh, dissolved H_2S , CO_2). This correction of surface values are important for water chemistry model validation.

A further possible application of the novel sensor and separation system is in the field of measurement-while-drilling (MWD). The principle of MWD measurements is known and disclosed in a vast amount of literature, including for example United States Patent No. 5,445,228, entitled "Method and apparatus for formation sampling during the drilling of a hydrocarbon well".

In FIG. 9, there is shown a wellbore **911** and the lower part of a drill string **912** including the bottom-hole-assembly (BHA) **910**. The BHA carries at its apex the drill bit **913**. It includes further drill collars that are used to mount additional equipment such as a telemetry sub **914** and a sensor sub **915**. The telemetry sub provides a telemetry link to the surface, for example via mud-pulse telemetry. The sensor sub includes the novel electro-chemical analyzing unit **916** as described above.

The analyzing unit **916** collects fluids from the wellbore via a small recess **917** protected from debris and other particles by a metal mesh.

5 During drilling operation wellbore fluid enters the recess **917** and is subsequently analyzed using sensor unit **916**. The results are transmitted from the data acquisition unit to the telemetry unit **914**, converted into telemetry signals and transmitted to the surface.

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A third application is illustrated in FIG. 10. It shows a Venturi-type flowmeter **1010**, as well known in the industry and described for example in the United States Patent No. 5,736,650. Mounted on production tubing or casing **1012**, the flowmeter is
15 installed at a location within the well **1011** with a wired connection **1013** to the surface following known procedures as disclosed for example in the United States Patent No. 5,829,520.

The flowmeter consists essentially of a constriction or throat
20 **1014** and two pressure taps **1018**, **1019** located conventionally at the entrance and the position of maximum constriction, respectively. Usually the Venturi flowmeter is combined with a densiometer **1015** located further up- or downstream.

25 The novel electro-chemical analyzing unit **1016** is preferably located downstream from the Venturi to take advantage of the mixing effect the Venturi has on the flow. A recess **1017** protected by a metal mesh provides an inlet to the unit.

30 During production wellbore fluid enters the recess **1017** and is subsequently analyzed using sensor unit **1016**. The results are transmitted from the data acquisition unit to the surface via wires **1013**.

35 Various embodiments and applications of the invention have been described. The descriptions are intended to be illustrative of

the present invention. It will be apparent to those skilled in the art that modifications may be made to the invention as described without departing from the scope of the claims set out below.